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DETERMINATION OF PGDN
IN
AQUEOUS SOLUTION

J.A. Hiltz - A.M. Quinn
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**DETERMINATION OF PGDN
IN
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Approved by B.F. Peters A/Director/Technology Division

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ABSTRACT

A procedure is described for the detection and quantitation of 1,2-propylene glycol dinitrate (PGDN), the monopropellant in Otto fuel 11, in aqueous solution down to the part per million (ppm) level. High Performance Liquid Chromatographic (HPLC) separation and ultraviolet (uv) detection of PGDN are utilized. The method developed is applied to evaluate the efficiency of organic solvent extractions of PGDN from waste water solutions generated at CFAD Bedford during maintenance of the MK37 and MK44 torpedoes. The results indicate that less than 1 ppm PGDN remains in solution following the extraction.

RÉSUMÉ

On décrit une méthode permettant de caractériser et de doser en solution aqueuse des quantités aussi faibles que 1 ppm (partie par million) de dinitrate de 1,2-propylèneglycol (PGDN), qui constitue le monergol du carburant Otto, 11. Cette méthode fait appel à la chromatographie liquide à haute performance (CLHP) pour la séparation et utilise l'ultraviolet (UV) pour la caractérisation. La méthode mise au point sert à évaluer l'efficacité du procédé utilisant un solvant organique pour extraire le PGDN des solutions d'eaux usées rejetées par le dépôt de munitions des Forces canadiennes de Bedford, au cours de l'entretien des torpilles MK37 et MK44. Selon les résultats, la solution renferme moins de 1 ppm de PGDN après l'extraction.

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ABBREVIATIONS

A - absorbance
A - area under an absorbance peak
b - pathlength of ultraviolet radiation
c - concentration of species in solution (moles/liter)
 ϵ - molar absorptivity
GC/MS - gas chromatography - mass spectroscopy
H - peak height
HPLC - high performance liquid chromatography
mm - millimeter (10^{-3} meter)
nm - nanometer (10^{-9} meter)
PGDN - 1,2-propylene glycol dinitrate
ppm - part per million
S/N - signal to noise ratio
STEL - short term exposure limit
T - transmittance
TLV - threshold limit value
TWA - time weighted average
uv - ultraviolet

1.0 INTRODUCTION

Otto fuel 11 is the liquid monopropellant used by the Canadian Forces in the MK37 and MK44 torpedoes. This monopropellant, named after its inventor Dr. Otto Reitlinger, is a mixture of three components; 1,2-propylene glycol dinitrate (PGDN), di-n-butyl sebacate, and 2-nitrodiphenylamine. PGDN is the actual propellant and makes up approximately 75% of Otto fuel 11 by weight, while di-n-butyl sebacate and 2-nitrodiphenylamine act as a desensitizing agent and a stabilizer respectively. The chemical structures and relative concentrations of the constituents of Otto fuel 11 are shown in Table 1.

PGDN has been found to be physiologically active and therefore a health hazard at relatively low concentrations in the air. Exposure to low levels of PGDN causes nasal congestion, headaches, dizziness, nausea, dilation of the blood vessels, decrease in blood pressure and labored breathing (1). The time weighted average-threshold limit value (TWA-TLV) in air has been set at 0.05 parts per million (ppm) and the short term exposure level-threshold limit value (STEL-TLV) at 0.1 ppm by the American Conference of Governmental Industrial Hygienists (2). However, Health and Welfare Canada has adopted more stringent TWA-TLV and STEL-TLV levels: they have been set at 0.02 and 0.05 ppm respectively (3). Methods that allow the determination of PGDN in air at the 0.02 ppm level (4) and the 0.05 ppm level (5) have recently been described.

Although Otto fuel 11 is contained in a butyl rubber fuel bladder in the torpedoes, leakage of the fuel can result in the contamination of the compartment in which the bladder is stored. As the Otto fuel 11 is seawater displaced from the fuel bladder, the seawater can become contaminated with Otto fuel 11 which has leaked from the containment system. During maintenance of torpedoes, the seawater/Otto fuel 11 suspension in this space is flushed out with fresh water to minimize the possibility of seawater accelerated internal corrosion. The resulting Otto fuel 11/water suspension is allowed to separate, leaving an aqueous layer contaminated with Otto fuel 11.

Two problems exist with this procedure. Firstly, no method is in place to monitor the concentration of Otto fuel 11, or more specifically PGDN, that remains in aqueous solution. Secondly, given that the aqueous solution is contaminated with PGDN, there are potential hazards associated with its disposal if the PGDN is not removed from the solution. In addition, no limit on the concentration of PGDN in aqueous solution that can safely be introduced to the environment has been established. As the solubility of PGDN is reported to be 0.13g/100 mL water (1300 ppm) (6) dumping of large volumes of saturated solutions of PGDN in water would introduce a considerable amount of this substance into the environment and could result in a potentially significant health and environmental hazard. An efficient extraction of PGDN from aqueous solution into an organic solvent would allow safe disposal of the PGDN

through burning of the solvent. The remaining water layer could then be discarded as uncontaminated waste.

As PGDN has a chromophore that absorbs in the ultraviolet region, ultraviolet spectrometry was proposed at DREA as a method for the detection and quantitation of PGDN in aqueous solution. The relationship between the response (absorbance or transmittance) of a chemical species and its concentration in solution is given by the Beer-Lambert law, or more simply, Beer's law, shown in Equation 1.1,

$$A = 2 - \log \% T = \epsilon bc \quad (1.1)$$

where A is the absorbance of the solution, T is the transmittance, ϵ is the molar absorptivity, b is the pathlength of the radiation through the solution in the sample cell, and c is the concentration of the solution in moles/liter.

The value of ϵ is characteristic of an absorbing species in a particular solvent and at a specified wavelength and is independent of both the pathlength of the radiation and the concentration of that species. As the pathlength of the radiation in the detector is fixed, the absorbance of a solution is directly proportional to concentration of a species in solution.

To utilize uv spectroscopy to measure the concentration of a compound in solution, it is necessary to separate it from other compounds that might absorb uv radiation at the selected analytical wavelength. Reversed phase high performance liquid chromatography (HPLC), commonly used to separate organic compounds in aqueous solution, was proposed. Reversed phase HPLC columns are characterized by non-polar packings, i.e., the affinity of the packing is greatest for non-polar compounds and consequently the polar compounds of a mixture elute first. By adjusting the polarity of the mobile phase, the retention times of the constituents of a mixture can be affected in such a way that the desired separation of the constituents is achieved.

Thus it appeared that reversed phase HPLC separation of the constituents of Otto fuel 11 coupled with uv detection and quantitation of PGDN would afford a convenient method to monitor PGDN concentration in waste water solutions from CFAD Bedford. This paper describes the development of such a procedure to measure the concentration of 1,2-propylene glycol dinitrate (PGDN) in aqueous solution at the part per million (ppm) level.

The method developed was subsequently used to evaluate the efficiency of organic solvent extractions of Otto fuel 11 from waste water solutions generated at CFAD Bedford during torpedo maintenance.

2.0 EXPERIMENTAL

2.1 Equipment and Reagents

All liquid chromatographic separations described in this report were carried out on a Varian model 5100 Liquid Chromatograph using a Varian MCH-10 (30 cm long x 0.4 cm. internal diameter) stainless steel reverse phase column. The MCH-10 packing was monomeric C-18 bonded on 10 micron silica gel. The separations were made under isocratic conditions (60% methanol-40% water) at a flow rate of 1.5 mL/min and a column temperature of 30°C. A 20 microliter injection loop was used in all analyses.

A Varian Varichrome variable wavelength ultraviolet-visible detector was used to monitor the compounds eluting from the HPLC column. The detector response was recorded on either a Varian model 9176 strip chart recorder or a Varian Vista 401 data station printer plotter. Detector response was measured as either the area under the absorbance peak (A) or the peak height at maximum absorbance (H). The area under the absorbance peak is a measure of the total absorbance of the PGDN that elutes from the column. Peak heights and peak areas were manually measured from the strip chart recorder trace while the area counts (integrated area) were obtained from a Varian CDS 111 integrator. The HPLC, uv detector, integrator, and strip chart recorder are shown in Figure 1.

Ultraviolet (uv) spectra of the pure components of Otto fuel 11 were recorded on a Perkin-Elmer Coleman 124 double beam ultraviolet spectrophotometer. The purity of the individual components was checked using infrared and mass spectrometry. The infrared spectra were obtained on a Perkin Elmer model 683 infrared spectrometer while the mass spectra were acquired on a Finnigan MAT 5100 gas chromatograph/mass spectrometer (GC/MS). Note Appendix A.

The water and methanol used as the mobile phase in the HPLC were HPLC grade (glass distilled) and were supplied by either Fisher Scientific or BDH Chemical Limited. The hexanes and petroleum ether (30-60°C) were supplied by BDH Chemical Limited (pesticide grade) and Fisher Scientific (ASC Certified) respectively.

Samples of di-n-butyl sebacate and 2-nitrodiphenylamine were purchased from Anachemia Limited and Aldrich Chemical Corporation respectively and used without further purification. A sample of pure PGDN was obtained by vacuum distillation from a sample of Otto fuel 11 (boiling point 59°C at 7 mm Hg).

2.2 Approach to the Analysis of 1,2-Propylene Glycol Dinitrate (PGDN) in Aqueous Solutions

Several steps were involved in the development of an analytical technique for the separation, detection and quantitation of PGDN in aqueous solution. They are as follows:

- 1) determination of the proper solvent mixture for the HPLC separation of the three components of Otto fuel 11,
- 2) identification of the optimum ultraviolet wavelength for the detection of 1,2-propylene glycol dinitrate in order to maximize the sensitivity of the detector, and
- 3) establishment of a calibration curve to relate concentration of PGDN in solution to detector response.

Ultraviolet (uv) spectra of the individual components of Otto fuel 11, namely, PGDN, di-n-butyl sebacate, and 2-nitrodiphenylamine are shown in Figures 2a through 2c respectively. It can be seen from Figures 2a and 2b that PGDN has an absorbance maximum around 205 nm and di-n-butyl sebacate has an absorbance maximum around 220 nm. Overlap of the absorbance peaks of these two components would preclude the use of a uv detector to quantitate PGDN unless the components were separated, because of possible interference effects.

Two criteria were set for the separation of the components of Otto fuel 11 by HPLC. The first was the complete (that is, baseline) separation of the constituents and the second was the elution of the three constituents within 15 minutes. To provide separation of the individual components of Otto fuel 11 and the desired elution time, HPLC using a reversed phase column and a binary solvent system (methanol-water) was chosen. Various methanol-water mixtures, including 90-10, 80-20, 70-30, 60-40, and 50-50 volume-volume solutions were trialed for the mobile phase at a flow rate of 1.5 mL/min.

Following the development of a separation procedure, an analytical wavelength for the quantitation of PGDN had to be selected. In the preliminary work to determine the mobile phase solvent mixture and retention times of the components of Otto fuel 11, the components were monitored at the wavelengths of maximum absorbance taken from the uv spectra shown in Figures 2a-2c. The optimum wavelength for monitoring the concentration of PGDN in aqueous solution was chosen by measuring the response of the uv detector to a 20 ppm solution of PGDN as the wavelength of the detector was varied from 225 nm to 200 nm in 5 nm increments. The wavelength that gave the maximum absorbance was selected as the analytical wavelength.

As the concentration of a uv absorbing species in solution is increased, the absorbance of the solution can increase to the point where

the response does not vary linearly with concentration. To utilize HPLC with ultraviolet detection to measure the concentration of PGDN in an aqueous waste water solution, it was necessary to determine the range over which the detector response increased linearly with PGDN concentration. It is general practice to work with solutions that provide more than 10% transmittance, which means A is always less than 1.0.

Calibration curves for the response of aqueous solutions of PGDN or Otto fuel 11 were prepared by injecting 20 microliter samples of standard aqueous solutions of Otto fuel 11 or PGDN into the HPLC and measuring the response of the uv detector. The standard solutions of PGDN in water and Otto fuel 11 in water were prepared by the serial dilution of stock 1000 ppm weight/volume (0.10g/100mL) solutions of either PGDN or Otto fuel 11 in water. These standard solutions contained 500, 200, and 20 ppm PGDN and 1000, 400, 200, 100, 50, and 20 ppm Otto fuel 11 in water. The absorbance at maximum peak height of the PGDN peak and the area under the PGDN peak were both measured and plotted against concentration.

The dynamic linear response range was found to be between 0 and 750 ppm PGDN. It was observed that solutions containing greater than 750 ppm PGDN had absorbances greater than one absorbance unit and the response of the detector fell off from that which would be predicted by more dilute solutions.

2.3 Extraction of PGDN from Aqueous Solution

The components of Otto fuel 11 are all soluble in common organic solvents. To utilize a particular solvent to extract PGDN from an aqueous solution the efficiency of the extraction must be determined. HPLC separation and uv detection of the components of Otto fuel 11 allow this to be accomplished. Waste water solutions from the flushing of torpedoes at CFAD Bedford were acquired and the solutions extracted with one of three solvents; varsol (CGSB 3-GP-8), petroleum ether (30-60° C), or hexanes. These solvents were selected because they are readily available, combust easily, and can be acquired at reasonable cost.

The procedure involved the extraction of 50 mL of waste water (samples obtained from CFAD Bedford) with 25 mL of a solvent, measurement of the concentration of PGDN remaining in solution, another extraction of the aqueous phase with 25 mL of solvent and determination of the concentration of PGDN remaining in the aqueous phase.

3.0 RESULTS AND DISCUSSION

3.1 HPLC Conditions

The results of varying the composition of the mobile phase used for the HPLC indicated that the 60-40 methanol-water mixture gave the desired

separation of the constituents of Otto fuel 11, i.e., no overlap of peaks and elution times were less than 15 minutes. The elution order and the retention times for the three components of Otto fuel 11 were PGDN (3.2 min), 2-nitrodiphenylamine (7.2 min), and di-n-butyl sebacate (14.9 min). Mobile phase solvent mixtures containing a higher proportion of methanol, i.e., 90-10, 80-20, and 70-30 methanol-water mixtures, did not result in complete separation of the components. The 50-50 methanol-water mixture gave a complete separation of the components of Otto fuel 11, but the components remained on the column for a longer period of time than with the 60-40 methanol-water mixture.

The wavelength of maximum absorbance for PGDN was determined to be 200 nm. Changing the wavelength of the detector to 198 or 202 nm resulted in a diminished response compared to that observed at 200 nm for a 20 ppm aqueous solution of PGDN.

3.2 Analytical Curves for Response of PGDN in Aqueous Solution

A plot of concentration of PGDN in aqueous solution against area under the peak (A) for the data listed in Table 2 is shown in Figure 3. The increase in response of the detector was linear over the concentration range studied, i.e., 0 to 500 ppm, as evidenced by the excellent correlation coefficient ($r^2 = 0.999$) for the linear least squares best fit straight line for the plot. Figure 4 shows a plot of the concentration of PGDN against peak height (H) for the data listed in Table 2. As was observed in Figure 3, the correlation coefficient for this plot was excellent ($r^2 = 0.999$), indicating that the response was linear over the concentration range studied.

Separation of PGDN from the Otto fuel 11 mixture on the HPLC resulted in a detector response, i.e., peak shape, that was gaussian in form. Typically, the PGDN peak took 0.7 minutes to elute from the column, and the peak was 0.3 minutes wide at half height. Peak heights were measured at the maximum absorbance point of the eluting PGDN peak and were calculated by setting a detector response of 0.2 absorbance units equal to 100. The peak height of an absorbance peak might be expected to vary considerably from one injection to the next as peak shape and consequently peak height are dependent upon the profile of the PGDN as it elutes from the column. However, peak heights were found to vary only slightly from one injection to the next for any of the standard solutions which indicates reproducible elution kinetics.

The analytical working curves shown in Figures 3 and 4 were established using pure PGDN. However, the waste water solutions received for analysis contain Otto fuel 11 in solution. Figure 5 shows a plot of concentration of PGDN in an aqueous Otto fuel 11 solution against A for the data listed in Table 3. The concentration of PGDN in each standard solution was calculated by multiplying the weight of Otto fuel 11 added to the solution by 0.75, the approximate weight fraction of PGDN in Otto fuel 11. The excellent correlation coefficient ($r^2 = 0.999$) found for

this plot indicates that the detector response is linear over the concentration range studied, i.e., 0 to 750 ppm. Figure 6 shows a plot of the concentration of PGDN in Otto fuel 11 against peak height (H) at maximum absorbance for the data listed in Table 3. The correlation coefficient for this plot is excellent ($r^2 = 0.999$) again indicating that the response is linear with concentration over the concentration range studied.

To determine if any error would be introduced by using standard Otto fuel 11 solutions to establish an analytical working curve for the concentration of PGDN in waste water solutions, the analytical curves shown in Figures 4 and 6 were plotted on the same axis in Figure 7. The similarity of the slopes and intercepts for the two analytical curves indicates that the assumption that Otto fuel 11 is 75 % by weight PGDN is valid and Otto fuel 11 can be used to establish analytical working curves for PGDN concentration in aqueous solution.

3.3 Limit of Detection of PGDN in Aqueous Solution

The minimum detectable limit of a substance is often defined as the concentration of that substance that gives a signal (response) to noise ratio (S/N) greater than two. In this work, response was measured as either area under the PGDN absorbance peak or the height of the absorbance peak at maximum absorbance. For instance, it was found that a 15 ppm solution of PGDN gave a response of 0.023 absorbance units on the 0.1 absorbance unit scale and had a S/N ratio of greater than 23. A 1 ppm solution gave a peak height at maximum absorbance of 0.0015 units and a S/N of 2. This result suggested that concentrations of PGDN in the sub ppm level might be detected. However, at concentrations below 1 ppm, the noise increased to the point where the S/N was less than two and 1 ppm was taken as the detection limit.

3.4 Extraction of PGDN from Aqueous Solution

The results of the extractions of the two waste water samples received from CFAD Bedford (see Table 4) indicate that both hexane and petroleum ether (30 - 60°C) can be used to extract PGDN from aqueous PGDN contaminated waste water solutions. Petroleum ether was more efficient than hexane, i.e., 90% of the PGDN was removed in the first extraction compared to 83% with hexane, but two extractions of a waste water sample with either of these solvents left less than 1 ppm dissolved PGDN in solution.

Evaluation of the use of varsol to extract PGDN from aqueous waste water was more difficult. It was observed that water soluble constituents in some varsol fractions had retention times similar to PGDN and made quantitation of residual PGDN in these aqueous solutions difficult. However, as the makeup of varsol varies from one supplier to the next and often from one distillation to the next, two extractions of a waste water sample with varsol (that did not contain constituents with retention times similar to PGDN) were found to leave less than 1 ppm PGDN

in solution.

The solvent extractions described will greatly reduce the amounts of PGDN that are discharged into the environment. An example follows which serves to illustrate this point. If 500 gallons (2280 liters) of waste water containing 500 ppm PGDN are dumped without any cleanup, 1140 grams of PGDN are introduced into the environment. Solvent extraction of the same 500 gallons of waste water would reduce the amount of residual PGDN to less than 2 grams.

4.0 CONCLUSIONS

A method combining the use of HPLC separation of the components of Otto fuel 11 and uv detection and quantitation of PGDN in aqueous solution at the ppm level has been described. The method involves no sample preparation and yields results in fifteen minutes. It has been used to evaluate the efficiency of extractions of PGDN contaminated waste water solutions with three organic solvents; hexane, petroleum ether and varsol. The results indicate that less than 1 ppm PGDN remains in aqueous solution after two extractions with any of the solvents evaluated.

TABLE 1

The chemical structures and percentage by weight of the constituents of Otto fuel 11.

<u>Constituent</u>	<u>Chemical Structure</u>	<u>% by weight</u>
1,2-propylene glycol dinitrate	$ \begin{array}{c} \text{N O}_2 \\ \\ \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad / \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \backslash \\ \text{O} \quad \text{H} \quad \text{H} \\ \\ \text{NO}_2 \end{array} $	75.8 - 76.2
di-n-butyl sebacate	$ \begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \qquad \qquad \\ \text{C}_4 \text{H}_9 - \text{O} - \text{C} - (\text{CH}_2)_8 - \text{C} - \text{O} - \text{C}_4 \text{H}_9 \end{array} $	22.5
2-nitrodiphenylamine	$ \begin{array}{c} \text{Ph} \\ \\ 2 - \text{NO}_2 - \text{Ph} - \text{N} - \text{H} \end{array} $	1.4 - 1.6

TABLE 2

The Ultraviolet Response (either Integrated Area or Peak Height) of Standard Solutions of PGDN in Water.

<u>Concentration</u> <u>(ppm)</u>	<u>Integrated Area</u> <u>A</u>	<u>Peak Height*</u> <u>H</u>
20	17964	16.7
200	215977	160.0
500	538477	383.0

* peak heights - 100 is equal to 0.2 absorbance units

TABLE 3

The Ultraviolet Response (either Integrated Area or Peak Height) of Standard Solutions of Otto fuel 11 in Water

<u>Concentration</u> ppm		<u>Integrated Area</u> A	<u>Peak Height</u> H
<u>OF11</u>	<u>PGDN</u>		
20.0	15.0	15188	11.6
50.0	37.5	35079	28.0
100.0	75.0	71414	53.8
200.0	150.0	131991	110.8
400.0	300.0	293692	219.0
1000.0	750.0	725458	495.0

*peak heights - 100 is equal to 0.2 absorbance units

TABLE 4

The results of extractions of two PGDN contaminated waste water samples with hexanes, petroleum ether, and varsol.

<u>PGDN CONCENTRATION (ppm)</u>				
<u>Sample</u>	<u>Solvent</u>	<u>Initial</u>	<u>1st extraction</u>	<u>2nd extraction</u>
1	Hexane	168	17	<1
2	"	288	29	<1
1	Pet ether	168	29	<1
2	"	288	50	<1
1	varsol	168	20	<1

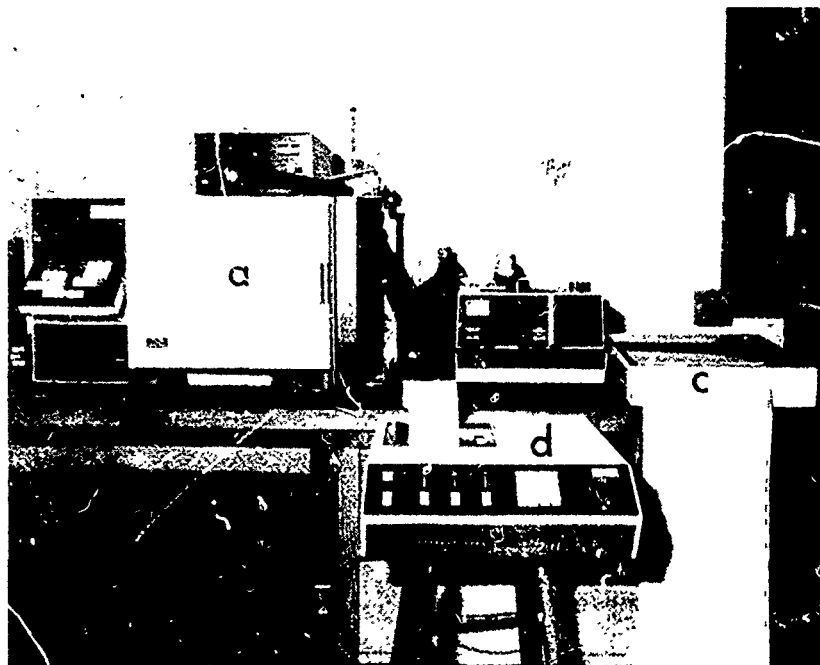


Figure 1 - The apparatus used in this work:
a) Varian model 5000 HPLC
b) variable wavelength ultraviolet detector
c) strip chart recorder
d) integrator

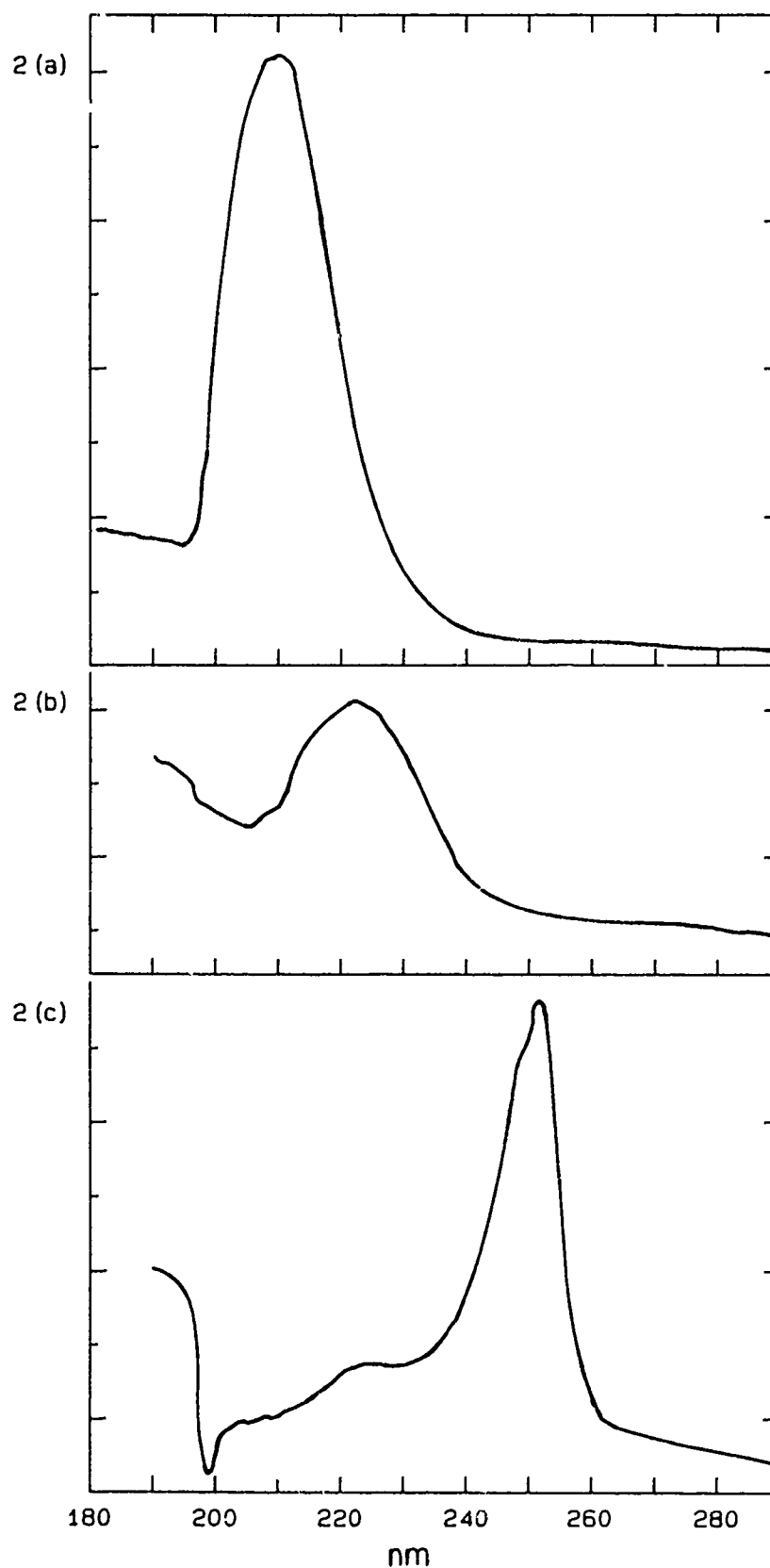


Figure 2a to 2c - The ultraviolet spectra of a) 1,2-propylene glycol dinitrate (PGDN), b) di-n-butyl sebacate, and c) 2-nitrodiphenylamine in 60% methanol - 40% water.

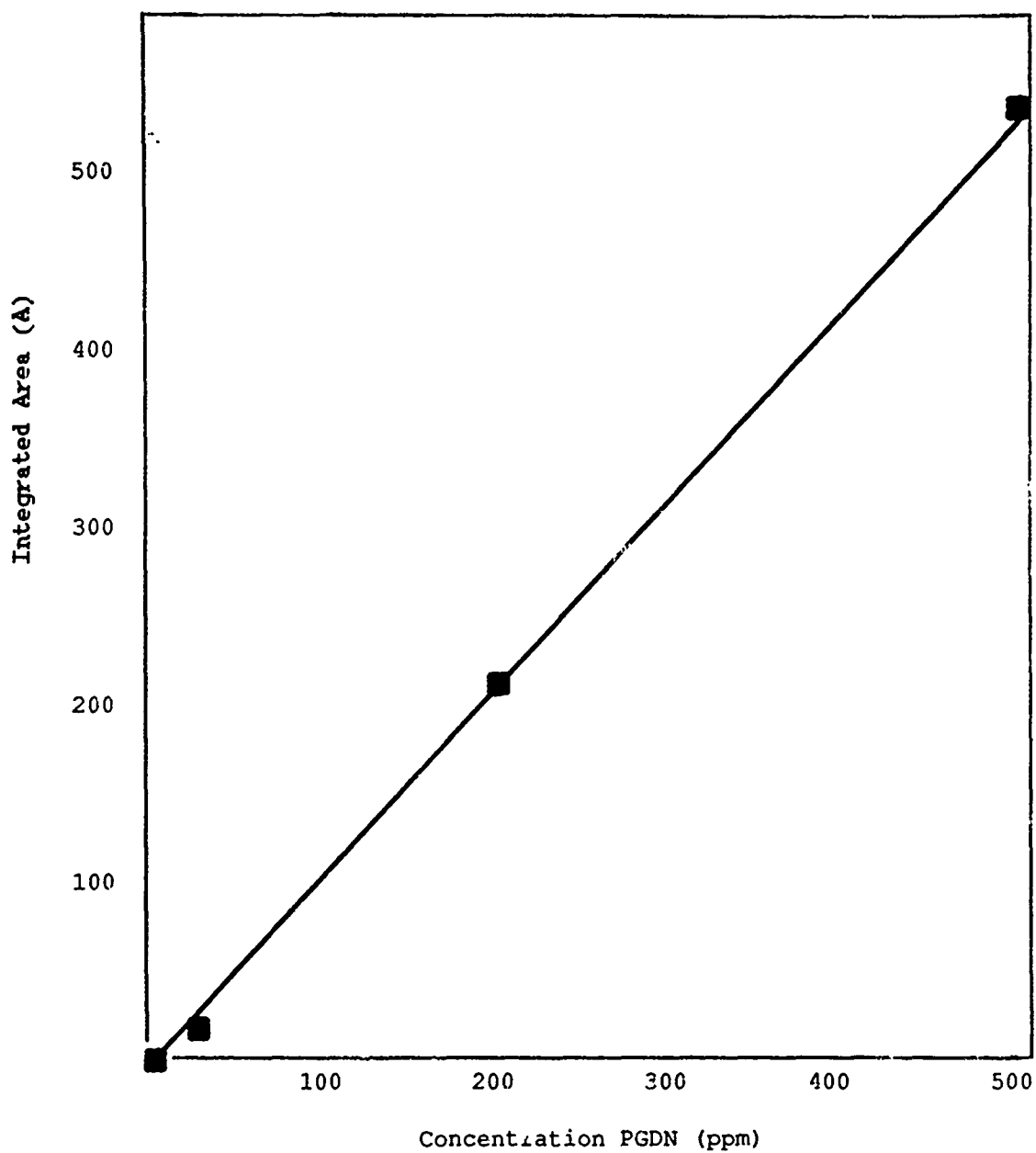


Figure 3 - Plot of the concentration of PGDN against uv absorbance (integrated area (A) of the absorbance peak) for a series of standard solutions of PGDN in water

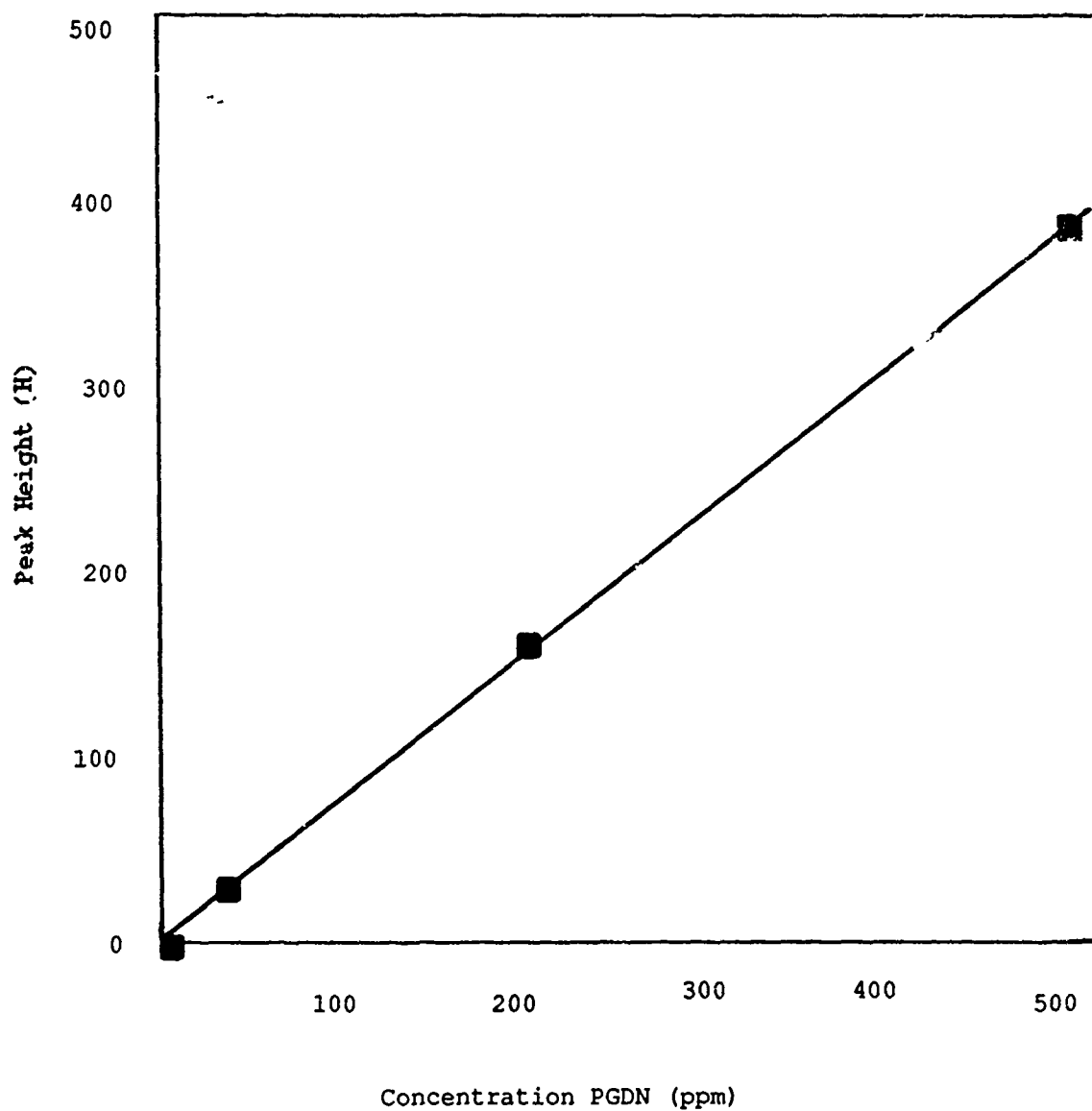


Figure 4 - Plot of the concentration of PGDN against uv absorbance (measured as peak height) for a series of solutions of PGDN in water.

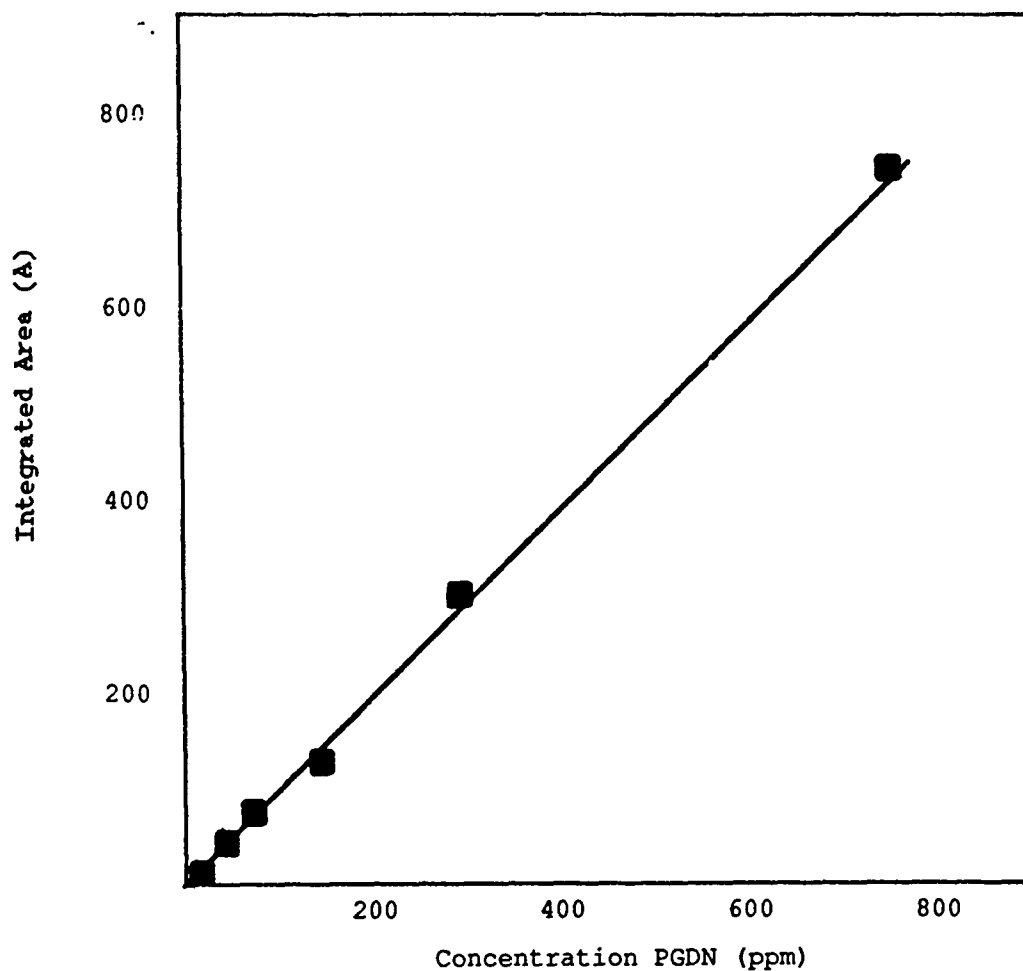


Figure 5 - Plot of the concentration of PGDN against integrated area (A) of the uv absorbance peak for a series of standard solutions of Otto fuel 11 in water.

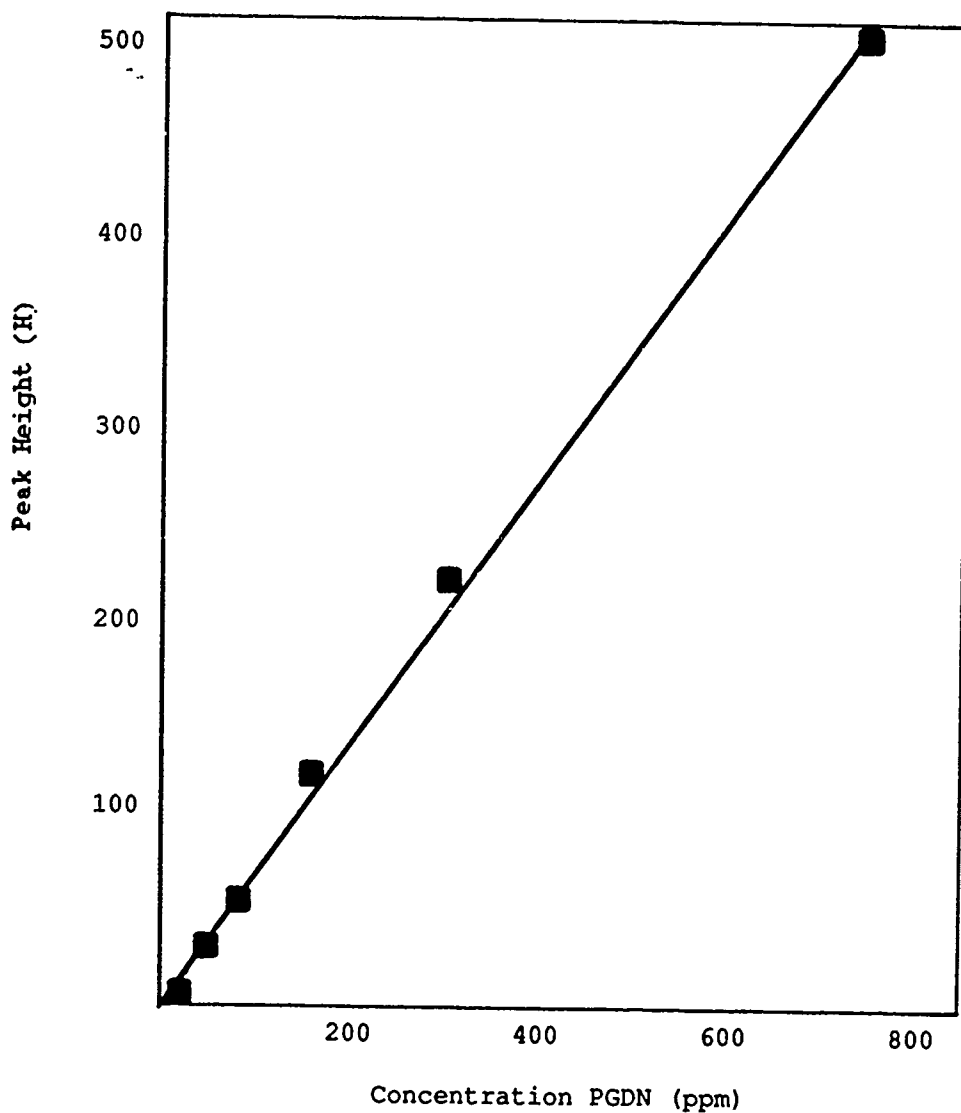


Figure 6 - Plot of the concentration of PGDN against peak height (H) of the uv absorbance for a series of standard solutions of Otto fuel 11 in water.

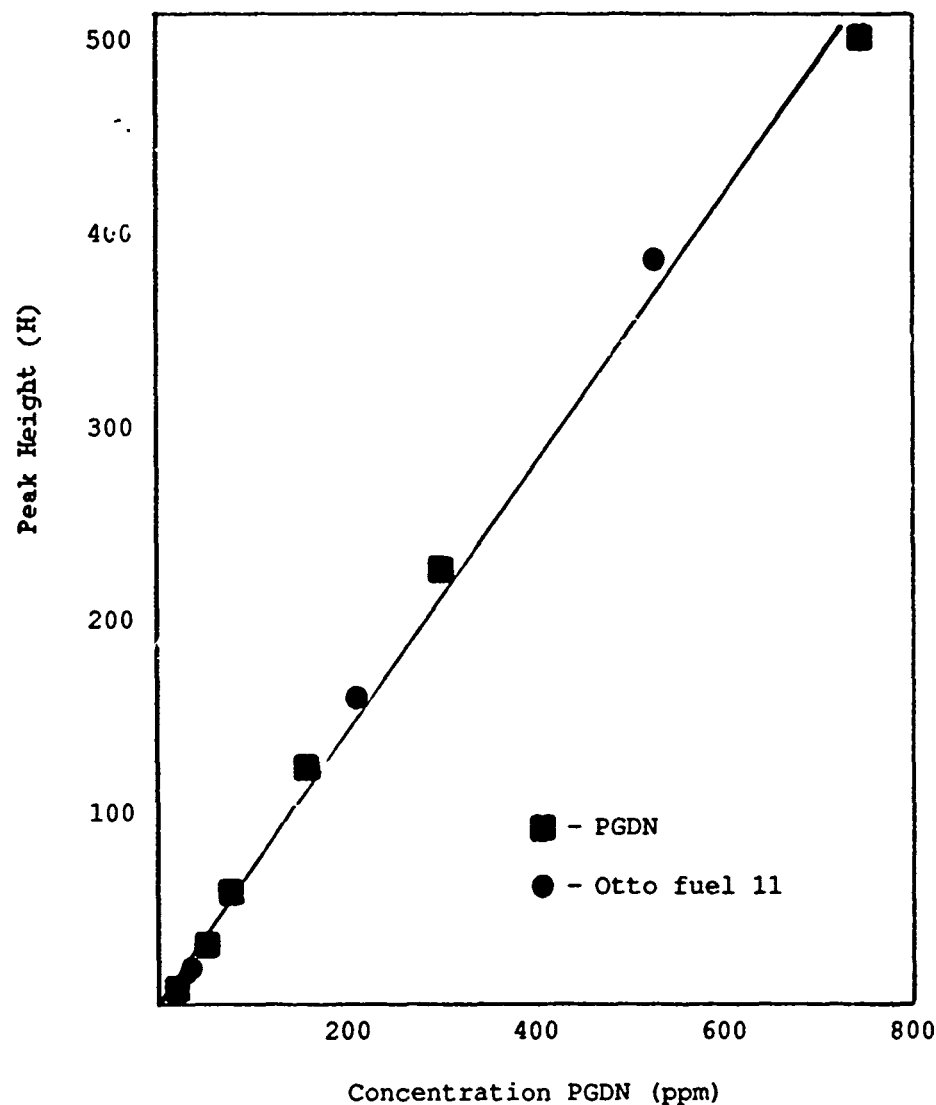


Figure 7 - Plot of the concentration of PGDN in series of standard solutions of PGDN and Otto fuel 11 in water against the Peak Height (H) of the uv absorbance.

APPENDIX A

This appendix includes the results of analytical procedures used to confirm the identity of PGDN. Infrared spectroscopy was utilized to characterize the presence/absence of nitrate ($-\text{ONO}_2$) and carbonyl ($-\text{OC}-$) functional groups. Mass spectrometry was utilized to verify the presence of PGDN. The Figures show the following spectra:

- A1. Infrared spectrum of Otto fuel 11 showing the absorption bands at 1620 and 1280 cm^{-1} for nitrate ($-\text{ONO}_2$) and a band at 1710 cm^{-1} for carbonyl ($-\text{CO}-$).
- A2. Infrared spectrum of di-n-butyl sebacate showing the absorption band at 1710 cm^{-1} due to this compound.
- A3. Infrared spectrum of 1,2-propylene glycol dinitrate showing absorption bands at 1620 and 1280 cm^{-1} due to this compound.
- A4. Mass spectrum of 1,2-propylene glycol dinitrate showing the fragmentation pattern for this compound.

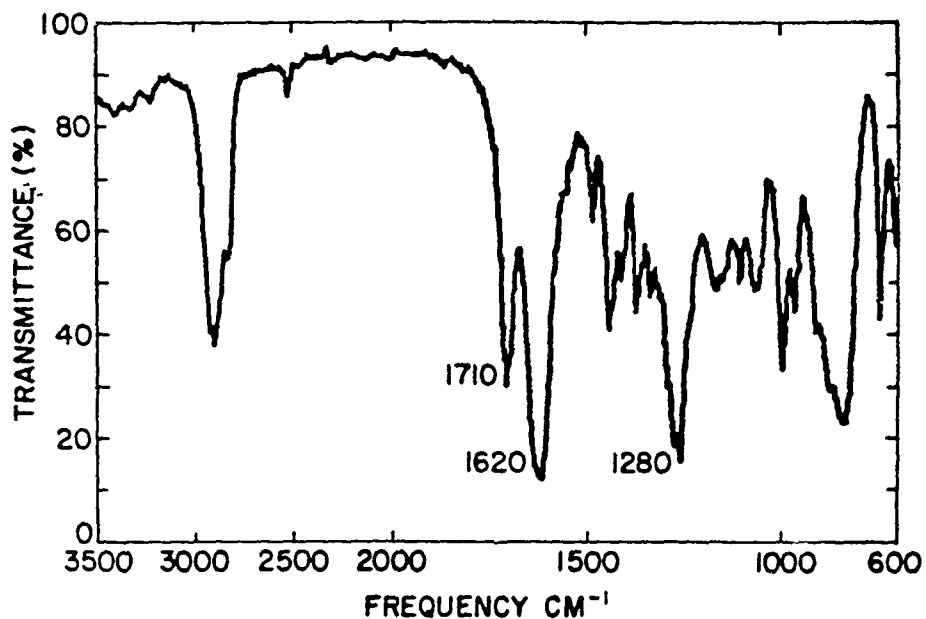


Figure A1: Infrared spectrum of Otto Fuel II showing absorption bands at 1620 and 1280 cm^{-1} for nitrate ($-\text{ONO}_2$) and a band at 1710 cm^{-1} for carbonyl ($-\text{CO}-$).

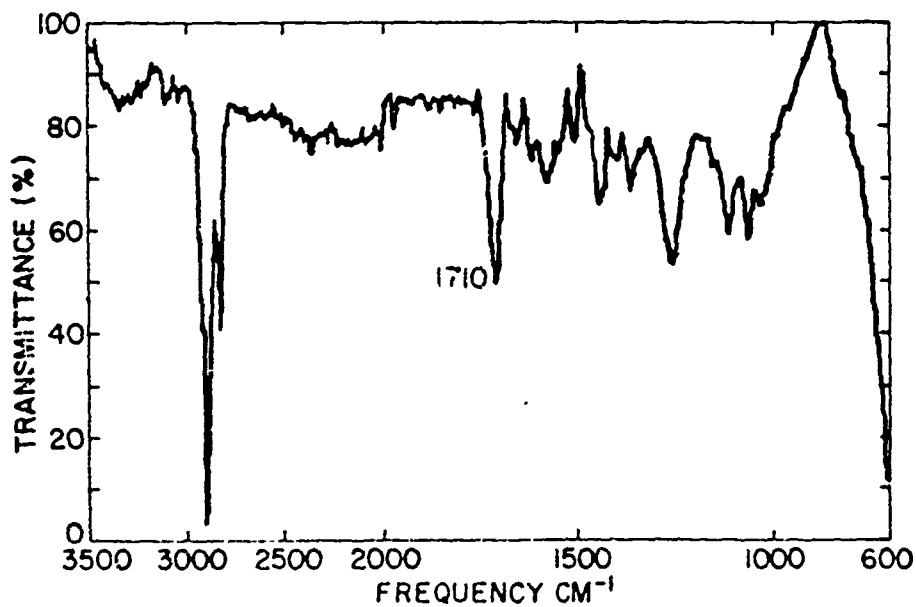


Figure A2: Infrared spectrum of di-n-butylsebacate showing absorption band at 1710 cm^{-1} due to this compound.

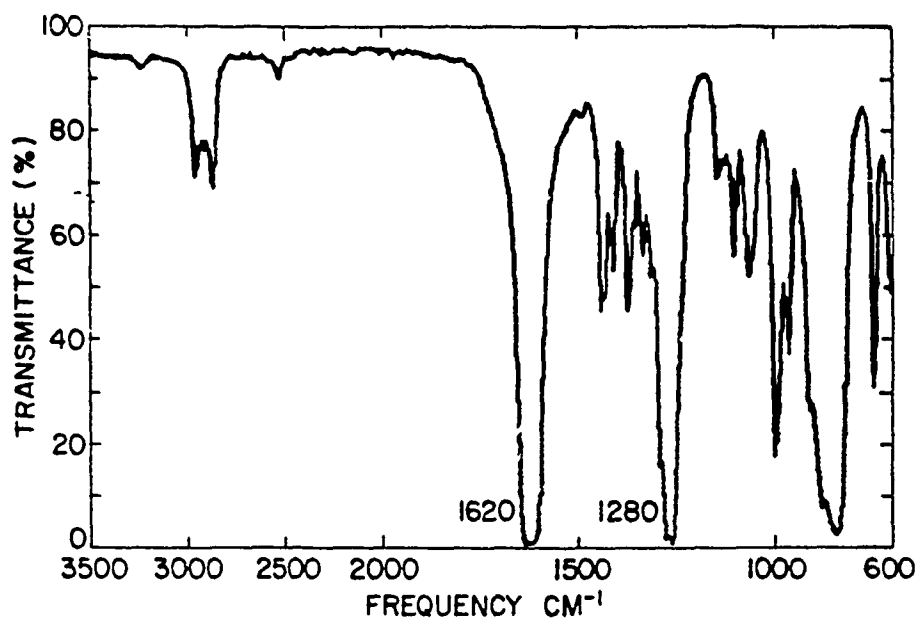


Figure A3: Infrared spectrum of 1,2-propylene glycol dinitrate showing absorption bands at 1620 and 1280 cm^{-1} due to this compound.

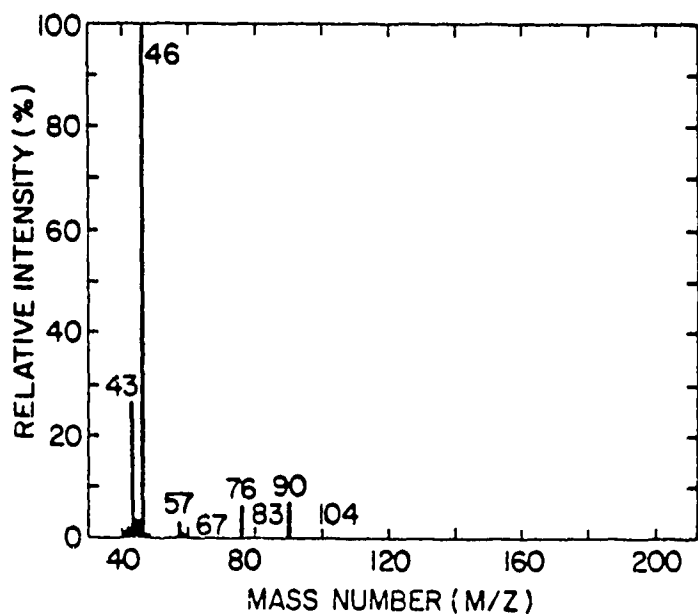


Figure A4: Mass spectrum of 1,2-propylene glycol dinitrate showing fragmentation pattern for this compound.

REFERENCES

1. R.D. Stewart, J.E. Peterson, P.E. Newton, C.L. Hake, M.J. Hosko, A.J. Lebrun and G.M. Lawton, "Experimental Human Exposure to Propylene Glycol Dinitrate", Toxicol. Appl. Pharmacol., 30, 377-395 (1974).
2. American Conference of Governmental Industrial Hygienists, "Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment", 1983.
3. M.M. Cohen, H.L. Johansen, J. Kirkbride, "A Study Concerning Employees Exposed to Otto Fuel 11", Health and Welfare Canada, April 1983.
4. R.M. Morchat and C.A. Shaw, "Gas Chromatographic Analysis of Otto fuel 11 in Air", DREA Technical Memorandum 84/E, April 1984.
5. B.D. Turnham, L.K. Yee, and G.A. Luoma, "Coated Piezoelectric Quartz Crystal Monitor for Determination of Propylene Glycol Dinitrate Vapor Levels", Anal. Chem., 57, 2120 (1985).
6. American Conference of Governmental Industrial Hygienists, "Documentation of the Threshold Limit Values for Substances in Workroom Air", Third Edition, 1977.

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<p>A procedure is described for the detection and quantitation of 1,2-propylene glycol dinitrate (PGDN), the monopropellant in Otto fuel 11, in aqueous solution down to the part per million (ppm) level. High Performance Liquid Chromatographic (HPLC) separation and ultraviolet (uv) detection of PGDN are utilized. The method developed is applied to evaluate the efficiency of organic solvent extractions of PGDN from waste water solutions generated at CFAD Bedford during maintenance of the MK37 and MK44 torpedoes. The results indicate that less than 1 ppm PGDN remains in solution following the extraction.</p>			

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KEY WORDS

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